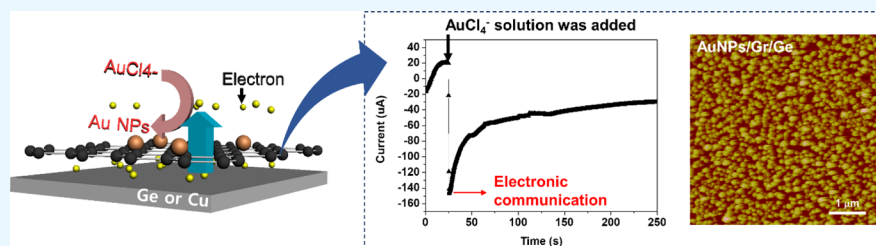


Spontaneous Formation of Gold Nanoparticles on Graphene by Galvanic Reaction through Graphene

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Supporting Information



ABSTRACT: We demonstrate an effective and facile method for the deposition of gold nanoparticles (AuNPs) on graphene by using spontaneous galvanic reaction. Despite the interest and importance of the hybrid structure of noble metal-deposited graphene has been considerably increased for its fundamental knowledge in chemical and physical sciences and for its various applications, the progress of this subject is very slow mainly because of the lack of synthetic methods for such structures, especially that are not free from chemical contamination and usage of complex and expensive equipment. Therefore, we developed a new method allowing chemically pure AuNPs/graphene hybrid structures employing galvanic reaction. The spontaneous galvanic reaction was derived from reductant/graphene/oxidant sandwich structures, such as Au ions/graphene/Ge wafer and Au ions/graphene/copper foil, by placing Au ion solution droplets on graphene transferred on a germanium wafer or as made graphene on Cu foil, respectively. According to scanning electron microscopy and atomic force microscopy results, it was confirmed that AuNPs were successfully formed on the graphene surface. This result implies two important points. One is that the formation of pure AuNPs on graphene is possible without using other chemicals frequently required for conventional NP preparation. The other one is that it was experimentally demonstrated that there are electronic communications between the oxidant and reductant that are separated by graphene, through which electrons can pass freely.

INTRODUCTION

The hybrid structures of metal nanoparticles (NPs) deposited on graphene have attracted a great deal of attention because of their potential applications in various fields in physics,¹ sensors,² catalysts,³ and so forth. Therefore, many researchers have contributed to develop methods to construct such hybrid structures by using external potential,⁴ laser,⁵ various additives,⁶ and so forth. However, most of the proposed methods have various limitations including cost ineffectiveness and process complexity because they require the use of many chemicals, additional equipment, or external energy source to apply. Among various electrochemical deposition processes, spontaneous galvanic reaction has been considered as one of the simplest and facile reactions that can form metal NPs when the metal source ions are brought into contact with the target substrate if their redox potential values are well matched.⁷ Previously, galvanic reaction was successfully employed to spontaneously form noble metal NPs, such as Au, Pt, and Pd NPs, on less noble metal or semiconductor substrates such as Cu and Ge without additives such as reducing agents, pH adjusters, and complexing agents.⁸ When the noble metal cations and the substrate are in contact, the electrons withdrawn from the reductant substrate by oxidation are

used to reduce the metal cations into the corresponding metal NPs on the substrate. In the p-type semiconducting single-walled carbon nanotube case, metal deposition could also be achieved spontaneously and directly by the galvanic reaction.⁹ However, in the graphene case, the galvanic reaction could not be applied because of its intrinsic semimetallic electronic structure. To overcome this limitation, we designed reductant/graphene/oxidant sandwich structures, so that the reductant and oxidant could cause the galvanic reaction and exchange charges through graphene and eventually form AuNPs on the surface of graphene.

RESULTS AND DISCUSSION

We chose germanium (Ge) and copper (Cu) as reductants that would reduce noble metal cations (Au³⁺) upon contact into the corresponding AuNPs according to thermodynamically favorable redox potential energy (Table 1).¹⁰

To achieve the spontaneous metal deposition on graphene, we first fabricated samples of the graphene/Ge structure by

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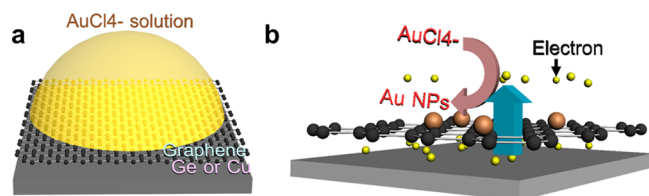
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Table 1. Electrochemical Redox Potential for Germanium/Gold and Copper/Gold Systems Available for Galvanic Reactions

system	redox couple	E° (V)	E°_{cell} (V)
Au/Ge	$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	+1.002	+0.878
	$\text{Ge} \rightarrow \text{Ge}^{4+} + 4\text{e}^-$	-0.124	
Au/Cu	$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	+1.002	+0.660
	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	-0.342	

transferring graphene that was separately synthesized by the chemical vapor deposition (CVD) process onto a Ge wafer substrate. (Detailed experimental method is described in the Method Section). After that, an aliquot of aqueous solution of AuCl_4^- (0.1 M) was dropped on graphene/Ge for 5 min (Scheme 1a). As a result, spherical AuNPs in a quite uniform

Scheme 1. (a) Experimental Design To Deposit AuNPs on Graphene as the Substrate (Ge or Cu)/Graphene/ AuCl_4^- Sandwich Structure; (b) Scheme of Spontaneous AuNPs Deposition on Graphene Mechanism That Shows Charge Communication between the Substrate (Ge or Cu) and AuCl_4^- Ions through Graphene



size (80–100 nm) were found on graphene as observed by optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) (Figures 1a,b and S1a). The size and uniformity of the resulting AuNP are largely affected by several reaction parameters including the concentration of AuCl_4^- , reaction time, and so forth. In addition, Raman spectra confirmed the successful transfer of graphene on the Ge substrate, and the formation of AuNPs was observed by enhanced Raman scattering because of AuNPs formed on the top of the graphene surface (Figure S2). The elemental composition of the AuNPs and substrate was investigated by X-ray photoelectron spectroscopy (XPS) (Figure S3).

To confirm the origin of the electrons from Ge rather than providing electrons from graphene itself, a series of control experiments were performed. We conducted the same reaction by using (1) the as-synthesized graphene on copper (graphene/Cu) instead of Ge, which also has matched the thermodynamically favorable redox potential (Table 1) to AuCl_4^- solution, and (2) the transferred graphene on SiO_2 (graphene/ SiO_2) to make sure that the origin of the electron is Ge or Cu, rather than graphene itself, thus to assure that graphene acts only as a window for electrons. In the graphene/Cu case, Cu foil has an advantage over Ge for preparing samples because Cu foil used for the growth of graphene by CVD still can be used without any extra treatment, which guarantees convenience and clean conditions. On the graphene/Cu samples, spherical AuNPs of 50–80 nm size were formed into a film (Figures 1c,d and S1b). Also, we observed high crystallinity of the resulting AuNPs by high-resolution transmission electron microscopy (HR-TEM) (Figure S4). On the other hand, in the case of graphene/ SiO_2 , no AuNP was found on graphene (Figure S5). This

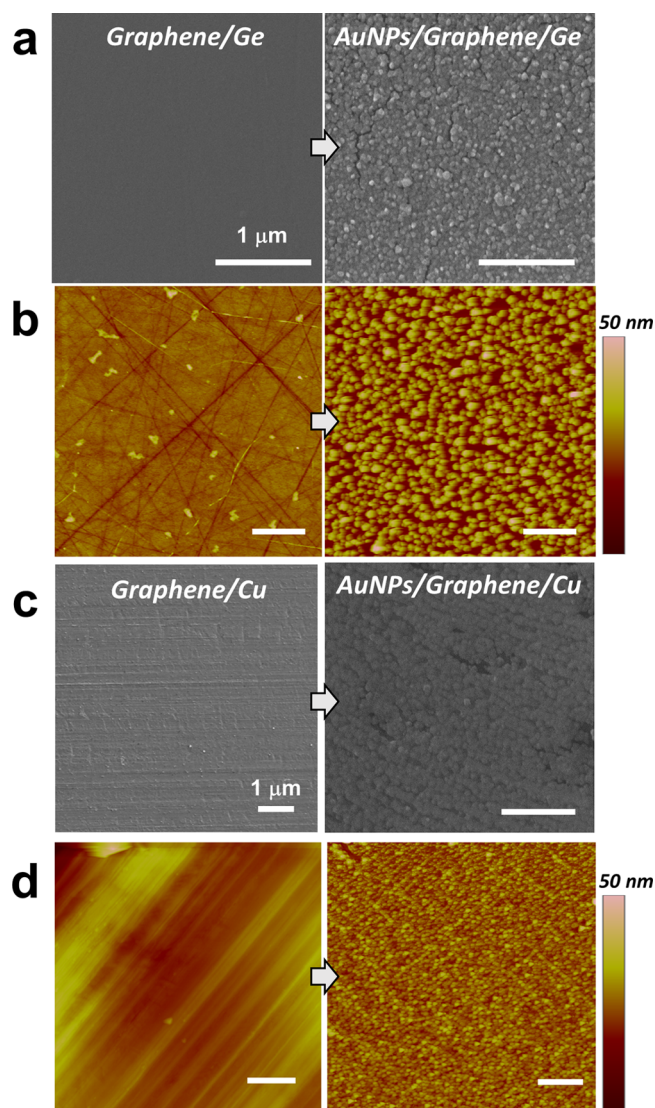


Figure 1. (a–d) SEM and AFM images of graphene/Ge and graphene/Cu after dropping AuCl_4^- solution.

clarifies that graphene itself does not involve in the reduction of AuCl_4^- , so the electrons used for the formation of AuNPs on graphene/Ge and graphene/Cu must come from Ge and Cu. In other words, the galvanic reaction that took place across the graphene could offer direct and facile metal NP deposition by using the electrons from Ge or Cu (Scheme 1b).

In general, the size of noble metal NPs formed by the spontaneous galvanic reaction is highly affected by the concentration of the oxidant solution.¹¹ Therefore, we examined the change in AuNP size by varying the concentration of AuCl_4^- solution (Figure 2a). The AuCl_4^- solutions at different concentrations of 0.5, 1.0, and 2.0 mg/mL resulted in the size increase of AuNPs from 49–106 and 85–141 to 289–690 nm, respectively. The trend indicates that the amount of electrons withdrawn from the Ge substrate differs depending on the concentration of the AuCl_4^- solution and it affects the size of the resulting AuNPs. Furthermore, to examine how many layers of graphene could be accessible for the spontaneous deposition by electrochemically generated electrons, the reaction was carried out with bilayer and trilayer graphene and exfoliated thick graphite. As a result, AuNPs grown on the bilayer graphene were similar to those of the

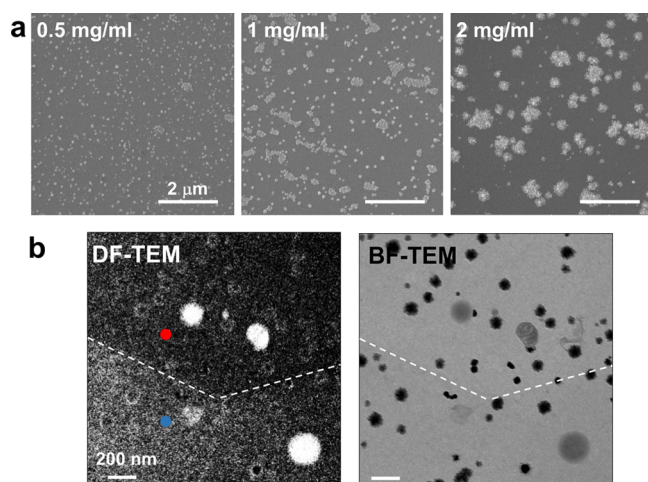


Figure 2. (a) SEM images of AuNPs which grown on graphene depending on the AuCl_4^- concentration. (b) Dark-field (left) and bright-field (right) TEM images of the AuNPs/graphene structure. Red and blue dots show different grain, and the white dotted line shows grain boundary.

monolayer graphene, and slightly larger AuNPs were grown on the trilayer graphene (Figure S6), but no AuNP was formed on the exfoliated graphite on Ge (Figure S7). This indicates that charge communication between the reductant and oxidant is available for bilayer and trilayer graphene but not beyond them.

The chance for the formation of AuNPs in the gap space between the graphene layer and Ge or Cu substrates was excluded because it is well known that most of large ions and molecules including solvents are impermeable to graphene.¹² Moreover, because all the reactions were performed by placing oxidant solution droplets on the top of graphene, there is no chance for the oxidant droplet to diffuse into the space between the graphene and substrate. Furthermore, to confirm whether AuNPs were formed on graphene grain or grain boundary, dark-field TEM measurement was conducted. As a result, we observed the area that shows different grains and grain boundaries (Figures S8 and 2b) and confirmed that AuNPs were formed on the graphene crystal domain rather than on the grain boundary.

Meanwhile, another direct evidence of charge communication between the reductant and oxidant through graphene was obtained from the electrical current flow through graphene. For this, we designed an electrochemical cell to measure the electrical current generated upon the galvanic reaction through graphene to elucidate the accurate and direct observation of the charge communication through graphene (Figure 3a). The electrochemical cell has a hole with a specific area to compare the accurate amount of electrons, and Ag/AgCl and Pt wire were used as the reference and counter electrode, respectively. (Detailed experimental method was described in Method section). When AuCl_4^- solution came into contact with Cu or graphene/Cu, the Cu was oxidized and AuNPs were formed. Because this means the electrons were extracted from Cu, we measured the current as a function of time using electrochemical current measurements. Because the redox reaction occurs spontaneously and immediately, the initial current measurement was performed in deionized (DI) water, and the change was measured upon adding AuCl_4^- solution while maintaining 0 V potential. To examine the tendency of

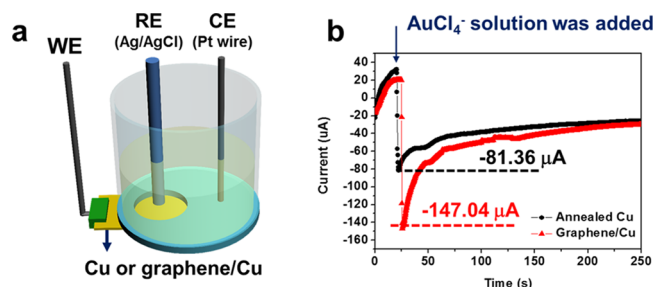


Figure 3. (a) Scheme of a lab-designed electrochemical cell for electrochemical current measurement. (WE: working electrode, RE: reference electrode, and CE: counter electrode). (b) Electrochemical current measurement of Cu and graphene/Cu as a function of time while maintaining 0 V potential.

electron generation and the influence of the substrate on passing, a series of control experiments were performed. We conducted the electrochemical current measurements by using (1) Cu and (2) graphene/Cu. As a result, from Cu and graphene/Cu cases, the instantaneous current increases to -81.36 and $-147.04 \mu\text{A}$ were observed, respectively, and then a gradual decrease was observed (Figure 3b). The instantaneous current increase may owe to extracting electrons from Cu, and the gradual decrease of the current indicates the accumulation of AuNPs. Also, the electrochemical current difference shown from Cu and graphene/Cu is believed to be originated from the native oxide layer present only on Cu. The oxide-free graphene/Cu shows a higher current level than the Cu-containing oxide layer. Furthermore, when the bias voltage was increased to more negative, the current also increased, which means the negative bias voltage accelerates the oxidation of Cu, allowing a higher current to flow (Figure S9). The concentration of AuCl_4^- solution also influences the current flow because a high concentration of AuCl_4^- drives higher mass transfer of Cu^{2+} ; hence, more electrons could be generated (Figure S10).

CONCLUSIONS

In conclusion, we demonstrated a direct and facile AuNPs deposition process on graphene by using galvanic reaction. An efficient electron transfer from the reductant to oxidant through graphene was induced by spontaneous galvanic redox reaction from reductant/graphene/oxidant sandwich structures and successfully resulted in AuNP deposition on graphene. It is also noteworthy that this result also confirmed the efficient charge communication through the graphene basal plane, by confirming that the charge transfer occurs through the graphene basal plane rather than through grain boundaries by performing TEM. Furthermore, the charge communication was proved by electrochemical current measurements that showed an immediate current increase. Our results have an importance as they not only suggest the simplest way for the fabrication of the metal NPs/graphene hybrid structure but also provide an opportunity to prove charge communication in a system divided by graphene, which can be further employed in various applications.

METHOD SECTION

General Information. All reagents were purchased from commercial sources and used without further purification. HAuCl_4 (Sigma-Aldrich > 99.9 %), Cu foil (Alfa Aesar, 0.025 mm thick, annealed, coated, 99.8%, metals basis), and Ge(110)

substrate (Crystal bank, 500 μm thick, N-type, undoped, >50 $\Omega\text{-cm}$ resistivity, single-side polished). All the SEM images were obtained by using a JEOL and AFM images using an atomic force microscope (Nanoscope III). Raman spectra were obtained using a confocal Raman spectrometer (WiTec), and XPS data were obtained at the Research Institute of Industrial Science and Technology (RIST, Korea) (VG ESCALAB 250, VG Scientific).

Synthesis of Graphene by CVD. A piece of Cu foil (Alfa Aesar, 0.025 mm thick, annealed, coated, 99.8%, metal basis) was purified by soaking it in acetic acid (25%) and dried by N_2 (99.999%) blowing. The Cu foil was located at the center of the 1 in. protection quartz tube inside a tube heating furnace under vacuum conditions ($\sim 4 \times 10^{-2}$ Torr), and H_2 gas (40 sccm, $\sim 12 \times 10^{-2}$ Torr) was flown for 10 min to flush the protection tube. After that, temperature was raised to 1050 $^\circ\text{C}$ and maintained for 10 minutes for annealing of Cu foil; then, the CH_4 gas (purity, vendor) was supplied for 20 min. Moreover, the Cu foil was fast cooled to 25 $^\circ\text{C}$ by opening the lid of the tube furnace, and CH_4 gas was turned off at 800 $^\circ\text{C}$.

Transfer Graphene from Cu to the Arbitrary Substrate. To transfer the graphene on a Ge substrate or graphene/AuNPs on a SiO_2 substrate, the poly(methyl methacrylate) (PMMA) solution (MicroChem Corp., 950 PMMA A5) was spin-coated on one side of the as-synthesized graphene or graphene/AuNPs on Cu foil and graphene on the other side was removed by using oxygen plasma (Femto Science, COVANCE-MPR). Cu was then etched by using ammonium persulfate aqueous solution and washed using DI water. The PMMA/graphene film was fished by a Ge(110) or SiO_2 substrate and heated at 180 $^\circ\text{C}$ for 2 h in air. Finally, PMMA was removed by soaking in acetone and annealed under Ar and H_2 flow for 1 h.

Electrochemical Current Measurements. A piece of Cu foil was annealed at 1050 $^\circ\text{C}$ for 10 min to equate conditions with the graphene/Cu sample. The electrochemical current measurements were performed using a Versastat 3.0. To measure the accurate and comparable current value, the electrochemical cell was designed to have a hole, which has a specific area to measure from the same exposed area. Ag/AgCl and Pt wire were used as the reference and counter electrode, respectively. The scan rate was 0.2 point per second, and the bias voltage was 0 V for 300 s.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02691.

Bright-field and dark-field optical microscopy images; Raman spectra of graphene/Ge; XPS spectra; HR-TEM image of AuNPs; SEM images; electron diffraction patterns, electrochemical current measurements; and AFM image (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AuNPs, gold nanoparticles; Cu, copper; Ge, germanium

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